

PATENT ABSTRACTS OF JAPAN

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(54) HOMOGENEOUS MICROPOROUS FILM MADE OF ULTRAHIGH-MOLECULAR WEIGHT POLYETHYLENE AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain the subject microporous film having a high strength and a moderate pore diameter by kneading and melting a mixture of ultrahigh-molecular weight polyethylene with inorganic fine powder and a specific plasticizer, molding the mixture into a sheetlike shape, extracting and removing the additives, drying the sheet and uniaxially drawing the dried sheet.

CONSTITUTION: A mixture of ultrahigh-molecular weight polyethylene having ≥ 2000000 viscosity-average molecular weight with inorganic fine powder and a plasticizer is molded into a sheetlike form while being kneaded and thermally melted. The inorganic fine powder and the plasticizer are respectively extracted and removed and the resultant sheet is dried and then drawn only in one axial direction to produce a microporous film. In the process, a mixed plasticizer of two kinds having 7.5-8.4 SP value and 8.5-9.5 SP value of plasticizers is used and the plasticizer having the 7.5-8.4 SP value is used in an amount of 10-150% based on the weight of the polyethylene to afford the objective microporous film having $\geq 40\%$ porosity, $\leq 450\text{sec}/100\text{cc}$ air permeability, $\geq 4000\text{kg/cm}^2$ modulus of elasticity in the machine direction, $\geq 400\%$ breaking elongation in the direction perpendicular to the machine direction, $2-10\text{kg/cm}^2$ bubble point in ethyl alcohol and ≤ 1.6 ratio of the maximum pore diameter to the average pore diameter.

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CLAIMS**[Claim(s)]**

[Claim 1] It is the fine porosity film which has the three-dimensional network which viscosity average molecular weight becomes from the ultra high molecular weight polyethylene which is 2 million or more. For 40% or more and air permeability, the elastic modulus of 450sec(s) / 100 cc or less, and the direction of a machine is [porosity] 4000kg/cm². Above, a bubble point [in / in whenever / breaking extension / of the direction of a machine, and the direction of a right angle / 400% or more and ethyl alcohol] -- 2kg/cm² - 10kg/cm² it is -- homogeneous fine porosity film [claim 2] made from ultra high molecular weight polyethylene with which the ratio of an average aperture and the maximum aperture is characterized by being 1.6 or less While viscosity average molecular weight carries out kneading / heating fusion of the mixture of the ultra high molecular weight polyethylene which is 2 million or more, non-subtlety fine particles, and a plasticizer, after fabricating in the shape of a sheet, In the manufacture approach of extract-removing, and drying non-subtlety fine particles and a plasticizer, respectively, extending only to 1 shaft orientations, and obtaining the fine porosity film SP value of this plasticizer uses at least two kinds of mixed plasticizers of 7.5-8.4, and 8.5-9.5. And SP value is characterized by the amount of plasticizers of 7.5-8.4 being this 10% - 150% of polyethylene weight. For 40% or more and air permeability, the elastic modulus of 450sec(s) / 100 cc or less, and the direction of a machine is [porosity] 4000kg/cm². Above, a bubble point [in /, in whenever / breaking extension / of the direction of a machine and the direction of a right angle / 400% or more and ethyl alcohol] -- 2kg/cm² - 10kg/cm² it is -- the manufacture approach of the homogeneous fine porosity film made from ultra high molecular weight polyethylene that the ratio of an average aperture and the maximum aperture is 1.6 or less

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the fine porosity film which consists of ultra high molecular weight polyethylene. Especially this invention relates to the fine porosity film made from polyethylene of the homogeneous ultrahigh molecular weight which has a three-dimensional network.

[0002]

[Description of the Prior Art] The fine porosity film is used as the separator, a separator, a membrane filter for electrolytic capacitors, etc. for cells. The separator and the separator for electrolytic capacitors for cells are expected the strong and homogeneous fine porosity film from the point of the assembly workability of a cell and an electrolytic capacitor, and dependability, and the fine porosity film with small electric resistance is especially demanded of the separator for nonaqueous electrolyte cells, such as a lithium cell, homogeneously [it is strong and].

[0003] Moreover, the membrane filter is expected the strong and homogeneous fine porosity film with a moderate aperture. In order to manufacture the strong fine porosity film, in the approach of porosity-izing with resin and a solvent, how to use and extend the polyethylene of ultrahigh molecular weight can be considered. For example, although it is high intensity, since the diameter of an average through tube is small, when it is not only suitable as a membrane filter which filters a lot of water, such as a water purifier, but uses as a separator for cells, the impregnating ability of the electrolytic solution is bad [it is indicated by JP,60-24203,A, and]. Moreover, a shaping sheet contracts sharply by plasticizer extract, and in order to have to carry out biaxial extension, at least, the elongation after fracture of an one direction is small, and is considered that the assembly workability of a cell is bad.

[0004] Furthermore, in order to have used as a separator of a lithium cell since thickness was thin as indicated by JP,60-136161,A, there was a problem from the point of safety. Moreover, although the manufacture approach of the fine porosity film with comparatively thick thickness which consists of ultra high molecular weight polyethylene is indicated by JP,63-273651,A, and it is high intensity similarly, a moderate aperture does not have, and permeability is small and it is not suitable as a membrane filter which processes a lot of water etc.

[0005] As the manufacture approach of other fine porosity film, there is the approach of carrying out extract removal and porosity-izing a plasticizer or a plasticizer, and a bulking agent after the phase separation of the mixture which consists of resin, a plasticizer, and a bulking agent. for example, it is thought that it is thought that the fine porosity film formed according to a common procedure and a common ingredient has high electric resistance, namely, its transparency resistance of water etc. is also high, a moderate aperture does not have and it is not suitable at least as a membrane filter, and it is not suitable for a separator since electric resistance is high as it is indicated by the detail in the letter, although it is JP,55-165573,A.

[0006] Furthermore, although there are JP,45-32097,B, JP,2-94356,A, etc., in any, viscosity average molecular weight is not indicated about the manufacture approach of 2 million or more fine porosity film made from ultrahigh molecular weight. This is because fabrication became difficult and

manufacture of the fine porosity film was completed up by the general approach, as it became ultrahigh molecular weight.

[0007] Moreover, if the fine porosity film which consists of mixture of ultra high molecular weight polyethylene and the amount polyethylene of giant molecules generally becomes mixture so that it may be compared by JP,60-242035,A and JP,3-105851,A; although JP,57-49629,A, JP,2-21559,A, etc. are indicated, fabrication nature will improve, but the strength of the fine porosity film is not a desirable approach, in order to fall remarkably and to obtain the strong fine porosity film.

[0008]

[Problem(s) to be Solved by the Invention] Although high intensity-ization is attained by using the polyethylene of ultrahigh molecular weight, the separator for lithium cells which needs the membrane filters and safeties for abundant water filtration etc. is expected the fine porosity film which has a moderate aperture and has whenever [moderate breaking extension] crosswise (the direction of a machine, and the direction of a right angle). However, the expected fine porosity film was not obtained from problems, such as lowness of the workability of ultra high molecular weight polyethylene.

[0009]

[Means for Solving the Problem] In the fine porosity film made from polyethylene of ultrahigh molecular weight, this invention person was high intensity, it has a moderate aperture, and found out the homogeneous fine porosity film and its manufacture approach, and completed this invention. Namely, this invention is fine porosity film which has the three-dimensional network which viscosity average molecular weight becomes from 2 million or more ultra high molecular weight polyethylene. For porosity, the elastic modulus of 40% or more, air permeability 450sec / 100 cc or less, and the direction of a machine is 4000kg/cm². Above, a bubble point [in / in whenever / breaking extension / of the direction of a machine, and the direction of a right angle / 400% or more and ethyl alcohol] -- 2kg/cm² - 10kg/cm² it is -- it is the homogeneous fine porosity film made from ultra high molecular weight polyethylene characterized by the ratio of an average aperture and the maximum aperture being 1.6 or less.

[0010] As polyethylene as used in the field of this invention, viscosity average molecular weight is 2 million or more, and the copolymer of the crystalline homopolymer or ethylene which carried out the polymerization of the ethylene, and the propylene not more than 10 mol %, 1-butene, 4-methyl-1-pentene and 1-hexene is raised. Resin has the network structure in three dimensions, and a three-dimensional network means the structure where between the network structures of the resin forms the hole as a free passage hole.

[0011] When it uses as a separator for cells, as for porosity, it is desirable from a viewpoint of the impregnating ability of the electrolytic solution, and the internal resistance of a cell that it is 40% or more, and it is desirable that it is 50 more% or more. If porosity becomes 85% or more, the reinforcement of the fine porosity film will fall and handling top fault will be produced. air permeability -- 450sec / 100 cc or less -- desirable -- 300sec(s) -- 100 cc or less is 200sec(s) / 100 cc or less still more preferably. When the internal resistance of a cell becomes high too much, and a cell property is reduced, when air permeability uses as a separator for cells in 450sec(s) / 100 cc or more, and it uses as a membrane filter, filtration effectiveness becomes [permeability] low bad.

[0012] the elastic modulus of the direction of a machine (longitudinal direction) -- 4000kg/cm² the above -- desirable -- 5000kg/cm² the above -- further -- desirable -- 6000kg/cm² it is . It is 4000kg/cm² when it uses as a separator for cells. Below, it is inferior to assembly workability and productivity, and it is thought that practicality is low. Whenever [breaking extension / of the direction of a machine and the direction of a right angle (cross direction)] is 500% or more still more preferably 450% or more preferably 400% or more. Although a reason is not certain, if this elongation after fracture becomes 400% or less, when carrying out pleating of this fine porosity film with a nonwoven fabric, it becomes easy to split in the direction of a machine.

[0013] Moreover, if whenever [breaking extension] becomes 400% or less, by being in the inclination which the internal short circuit of a cell increases, and having moderate elongation crosswise at the time of cell assembly, although a reason is not certain, it will be hard to split in the direction of a machine,

and it will be thought that a hole cannot become large easily. the bubble point in ethyl alcohol -- 2kg/cm² - 10kg/cm² -- desirable -- 3kg/cm² - 9kg/cm² -- further -- desirable -- 4kg/cm² - 8kg/cm² it is . The bubble point in ethyl alcohol is 2kg/cm². Below, the aperture of the fine porosity film is large, and when it uses as a membrane filter, it worries about the leak of a bacillus, and when it uses especially for the separator of a lithium cell, it worries about generating of an internal short circuit. Moreover, the bubble point in ethyl alcohol is 10kg/cm². Above, when the aperture of the fine porosity film is too small and uses as a membrane filter, permeability becomes small, filtration effectiveness is bad, and when it uses as a separator for cells, there is a possibility of causing the fall of the impregnating ability of the electrolytic solution.

[0014] It is thought that the homogeneity of the internal resistance of a cell is required for reservation of safety, and in desiring fine porosity film homogeneous [when using as a membrane filter] in order to secure positive disinfection nature and using especially as a separator of a lithium cell, similarly, homogeneous fine porosity film is desired, and when the ratio of an average aperture and the maximum aperture becomes 1.6 or more, anxiety is in homogeneity. Preferably, it is 1.4 or less still more preferably 1.5 or less.

[0015] Although especially thickness is not specified in this invention, the point of the dependability as a membrane filter and the dependability as a separator for cells to 15 micrometers - 60 micrometers are desirable. 20 micrometers - 50 micrometers are 25 micrometers - 45 micrometers still more preferably more preferably. When set to 15 micrometers or less, it is inferior to the filtration precision (the depth effectiveness) of the direction of thickness, and there are worries about an internal short circuit in the separator for cells. Since permeability falls as a membrane filter and internal resistance increases as a separator for cells in 60 micrometers or more, it is not desirable.

[0016] It is the fine porosity film which has the three-dimensional network which the viscosity average molecular weight which this invention indicates becomes from 2 million or more ultra high molecular weight polyethylene. Air permeability 40% or more 450sec(s) / 100 cc or less, [thickness] [15 micrometers - 60 micrometers and porosity] The elastic modulus of the direction of a machine is 4000kg/cm². Whenever [breaking extension / of the direction of a machine and the direction of a right angle] above 400% or more, the bubble point in ethyl alcohol -- 2kg/cm² - 10kg/cm² it is -- the homogeneous fine porosity film made from ultra high molecular weight polyethylene with which the ratio of an average aperture and the maximum aperture is characterized by being 1.6 or less is the optimal as a separator for lithium cells.

[0017] Furthermore, the configuration of the hole currently punctured on this fine porosity film front face is considered that an ellipse form is desirable. When it uses as a membrane filter, if puncturing of this fine porosity film front face is an ellipse form, it will compare circularly and it will be thought that it is hard to carry out blinding that a filtration life is long, 1.3 or more have the desirable ratio of the major axis and minor axis of this ellipse form, and, as for this, 1.5 or more are still more desirable. After viscosity average molecular weight fabricates the fine porosity film of this invention in the shape of a sheet, carrying out kneading / heating fusion of the mixture of 2 million or more ultra high molecular weight polyethylene, non-subtlety fine particles, and a plasticizer, In the manufacture approach of extract-removing, and drying non-subtlety fine particles and a plasticizer, respectively, extending only to 1 shaft orientations, and obtaining the fine porosity film SP value of this plasticizer is manufactured by the manufacture approach that SP value is characterized by the amount of plasticizers of 7.5-8.4 being this 200% or less of polyethylene weight, using at least two kinds of mixed plasticizers of 7.5-8.4, and 8.5-9.5.

[0018] Moreover, in two or more kinds of only chosen mixed plasticizers, the fine porosity film which has a strong and moderate aperture is not obtained. Using two or more kinds of plasticizers which are indicated by this invention and which were chosen especially, by restricting at least one kind of amount of plasticizers, fabrication is easy and the homogeneous fine porosity film made from ultra high molecular weight polyethylene which fitted the membrane filter, the separator for cells, etc. with high intensity and a moderate aperture by extension of only 1 shaft orientations is obtained. Not only industrial production top economical efficiency is high, but since it has moderate elongation after

fracture crosswise (the direction of a right angle of the extension direction), that have a moderate aperture by extension of only 1 shaft orientations, and the high intensity fine porosity film is especially obtained in the extension direction has the description referred to as being hard to split in the direction of a machine.

[0019] Polyethylene, a plasticizer, and non-subtlety fine particles are extracted and dried after mixing and shaping, and, specifically, it manufactures by extending further. As non-subtlety fine particles, fines silicic acid; a calcium silicate, aluminum silicate, a calcium carbonate, fines talc, etc. are raised. For example, after making the mixed presentation of polyethylene, non-subtlety fine particles, and a plasticizer into 10 - 40 % of the weight, 5 - 35 % of the weight, and 20 - 80 % of the weight, respectively and mixing with the usual mixers, such as a Henschel mixer, it kneads with melting kneading equipments, such as an extruder, and the obtained kneading object is fabricated in thickness of 80 micrometers - 600 micrometers by extrusion molding etc. Furthermore, extract removal of the plasticizer is carried out using a solvent from this moldings, and after the extract solvent of non-subtlety fine particles extracts non-subtlety fine particles continuously, the fine porosity film excellent also in extension of only 1 shaft orientations is obtained.

[0020] As a solvent of a plasticizer, common organic solvents, such as chlorine-based hydrocarbons, such as ketones, such as alcohols, such as a methanol and ethanol, an acetone, and MEK, and 1,1,1-trichloroethane, are used. SP value used for this invention is raised for straight mineral oil, such as a liquid paraffin and process oil, etc. as a plasticizer of 7.5-8.4.

[0021] Moreover, SP value is raised for DBP, DOP, DNP, DBS, TBP, etc. as a plasticizer of 8.5-9.5. SP value is desirable 200% from 5% of polyethylene weight, and the amount of plasticizers of 7.5-8.4 is 50% - 100% most preferably 35% to 100% still more preferably 15% to 150%. If this amount of plasticizers becomes 200% or more, at 5% or less, the fine porosity film which has a moderate aperture is not obtained, but manufacture is [a moldability is bad and] difficult.

[0022] in order for the amount of this mixed plasticizer to have miscibility and a moderate aperture -- this mixture (polyethylene, plasticizer, and inorganic pulverized coal) weight [50% of] - it is 60% - 120% still more preferably 55% to 150% preferably 180%. If the fine porosity film of an aperture with this amount of mixed plasticizers moderate at 50% or less is not obtained but becomes 180% or more, the miscibility of polyethylene, a plasticizer, and inorganic pulverized coal will fall, and it will become difficult [fabrication].

[0023] Moreover, it is necessary to extend extension only to 1 shaft orientations. Although it is also possible to carry out biaxial stretching with a natural thing, there is a problem referred to as that moderate elongation after fracture is not obtained crosswise.

[0024]

[Example] Hereafter, although an example explains this invention, this invention is not limited to the following example. In addition, a measuring method is shown below.

- (1) It measured with the dial gage of the 1 micrometer of the thickness minimum graduations.
- (2) The sample of a porosity the angle of 10cm was started, the weight and thickness at the time of the weight and the bone dry at the time of the water of a sample were measured, and it asked from the bottom type.

[0025] Porosity = (hole volume / fine porosity film volume) x100 (%)

Hole volume = ([wet weight g]-oven dry weight [g]) the consistency of /water [g/cm³]

Fine porosity film volume = 100x thickness [cm]

(3) Bubble point ASTM The bubble point in ethanol was measured based on E-128-61.

(4) Air permeability JIS Based on P-8117, the time amount required by the marked-line graduations 0-100 was measured by the stopwatch using B mold gar rhe type Denso meter made from an Oriental energy machine.

(5) Using the form autograph AG-A mold by elastic-modulus Shimazu, the magnitude of a test piece performed the tension test in the distance between chucks of 5mm, and speed-of-testing 200 mm/min by width-of-face [of 10mm] x die length of 100mm, and measured the elastic modulus.

[0026] The cross section was computed by the thickness x film width measured by (1) term.

(6) Whenever [**** breaking extension], using the Shimazu form autograph AG-A mold, the magnitude of a test piece performed the tension test in the distance between chucks of 50mm, and speed-of-testing 200 mm/min by width-of-face [of 10mm] x die length of 100mm, calculated the amount of elongation from a chart to fracture, and computed by the bottom type.

[0027] It is =(amount [mm] of elongation-50[mm] to fracture)/50[mm] x100[%] whenever [**** breaking extension].

(7) Average aperture ASTM It asked by the half dry cleaning method based on F-316-70.

(8) The maximum aperture ASTM According to E-128-61, it computed from the bubble point in the inside of ethanol.

(9) Using the viscosity-average-molecular-weight decalin, viscosity was measured with the UBEROZE mold viscosity mold at the measurement temperature of 135 degrees C, and viscosity average molecular weight was calculated by the formula of Chiang.

[0028]

[Example 1] 17 % of the weight of ultra high molecular weight polyethylene, 18 % of the weight of fines silicic acid, 50 % of the weight of dioctyl phthalates, and 15 % of the weight of liquid paraffins of viscosity average molecular weight 3 million were mixed with the Henschel mixer, and the mixture concerned was fabricated by the film manufacturing installation which attached the T die of 450mm width of face in phi30mm twin screw extruder with a thickness of 200 micrometers in the shape of film.

[0029] The fabricated film was immersed for 10 minutes into 1,1,1-trichloroethane, after extracting dioctyl phthalate, it dried, it was immersed for 60 minutes into 60 more-degree C 25% caustic alkali of sodium, and after extracting fines silicic acid, it was dried. Furthermore, this fine porosity film was extended so that thickness might be set to 30 micrometers - 40 micrometers by the heated 125-degree C 1 shaft roll drawing machine, and heat treatment was performed for 5 seconds under the 115-degree C ambient atmosphere.

[0030] The property of the obtained fine porosity film is shown in Table 1.

[0031]

[Example 2] It carried out like the example 1 except having used the ultra high molecular weight polyethylene of viscosity average molecular weight 2 million. The result is shown in Table 1.

[0032]

[Example 3] It carried out like the example 1 except 35 % of the weight of dioctyl phthalates, and 30 % of the weight of liquid paraffins. The result is shown in Table 1.

[0033]

[Example 4] It carried out like the example 1 except 57 % of the weight of dioctyl phthalates, and 8 % of the weight of liquid paraffins. The result is shown in Table 1.

[0034]

[Example 5] It carried out like the example 1 except having mixed 18 % of the weight of ultra high molecular weight polyethylene, 17 % of the weight of fines silicic acid, 48 % of the weight of dioctyl phthalates, and 17 % of the weight of liquid paraffins of viscosity average molecular weight 3 million with the Henschel mixer. The result is shown in Table 1.

[0035]

[The example 1 of a comparison] Other than 30 % of the weight of dioctyl phthalates, and 35 % of the weight of liquid paraffins, although it was going to carry out like the example 1, the miscibility in a Henschel mixer was bad and did not result in fabrication.

[0036]

[The example 2 of a comparison] It carried out like the example 1 except only the liquid paraffin having used 65 % of the weight as a plasticizer. The result is shown in Table 1.

[0037]

[The example 3 of a comparison] Fabrication was not able to be carried out although it was going to carry out like the example 1 except only dioctyl phthalate having used 65 % of the weight as a plasticizer.

[0038]

[The example 4 of a comparison] As a plasticizer, other than having used the acetyl tree n-butyl phthalate of the SP value 10.0 [about], although it was going to carry out like the example 1, fabrication was not able to be carried out instead of dioctyl phthalate.

[0039]

[The example 5 of a comparison] As a plasticizer, other than having used the G n-octyl tetrahydro phthalate of the SP value 7.2 [about], although it was going to carry out like the example 1, fabrication was not able to be carried out instead of the liquid paraffin.

[0040]

[The example 6 of a comparison] It carried out like the example 1 except having extended to biaxial this fine porosity film heated by 125 degrees C 3 time x 3 times using the tenter. The result is shown in Table 1.

[0041]

[Table 1]

	気孔率 (%)	透気度 (SEC/ 100CC)	M D 弹性率 (kg/cm ²)	CMD 破断伸度 (%)	パブル ポイント (kg/cm ²)	最大孔径 と平均 孔径比	膜 厚 (μm)
実施例1	72	180	8000	480	6.1	1.5	34
実施例2	72	180	7600	500	6.0	1.5	40
実施例3	65	170	8000	500	7.8	1.5	36
実施例4	70	170	7500	500	5.9	1.5	40
実施例5	68	170	8500	510	6.0	1.5	32
比較例1							
比較例2					10.0以上		
比較例3							
比較例4							
比較例5							
比較例6				300			

[0042]

[Effect of the Invention] According to the above-mentioned configuration, the fine porosity film which has a moderate aperture with high intensity is obtained, and as reliable filtration film, especially as a membrane filter, it is especially homogeneous, workability and safety are high as a separator for nonaqueous electrolyte cells, and it can apply as a separator which is low internal resistance and has the uniform property of low internal resistance.

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PRIOR ART

[Description of the Prior Art] The fine porosity film is used as the separator, a separator, a membrane filter for electrolytic capacitors, etc. for cells. The separator and the separator for electrolytic capacitors for cells are expected the strong and homogeneous fine porosity film from the point of the assembly workability of a cell and an electrolytic capacitor, and dependability, and the fine porosity film with small electric resistance is especially demanded of the separator for nonaqueous electrolyte cells, such as a lithium cell, homogeneously [it is strong and].

[0003] Moreover, the membrane filter is expected the strong and homogeneous fine porosity film with a moderate aperture. In order to manufacture the strong fine porosity film, in the approach of porosity-izing with resin and a solvent, how to use and extend the polyethylene of ultrahigh molecular weight can be considered. For example, although it is high intensity, since the diameter of an average through tube is small, when it is not only suitable as a membrane filter which filters a lot of water, such as a water purifier, but uses as a separator for cells, the impregnating ability of the electrolytic solution is bad [it is indicated by JP,60-24203,A, and]. Moreover, a shaping sheet contracts sharply by plasticizer extract, and in order to have to carry out biaxial extension, at least, the elongation after fracture of an one direction is small, and is considered that the assembly workability of a cell is bad.

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[0010] As polyethylene as used in the field of this invention, viscosity average molecular weight is 2 million or more, and the copolymer of the crystalline homopolymer or ethylene which carried out the polymerization of the ethylene, and the propylene not more than 10 mol %, 1-butene, 4-methyl-1-pentene and 1-hexene is raised. Resin has the network structure in three dimensions, and a three-dimensional network means the structure where between the network structures of the resin forms the hole as a free passage hole.

[0011] When it uses as a separator for cells, as for porosity, it is desirable from a viewpoint of the impregnating ability of the electrolytic solution, and the internal resistance of a cell that it is 40% or more, and it is desirable that it is 50 more% or more. If porosity becomes 85% or more, the reinforcement of the fine porosity film will fall and handling top fault will be produced. air permeability -- 450sec / 100 cc or less -- desirable -- 300sec(s) -- 100 cc or less is 200sec(s) / 100 cc or less still more preferably. When the internal resistance of a cell becomes high too much, and a cell property is reduced, when air permeability uses as a separator for cells in 450sec(s) / 100 cc or more, and it uses as a membrane filter, filtration effectiveness becomes [permeability] low bad.

[0012] the elastic modulus of the direction of a machine (longitudinal direction) -- 4000kg/cm² the above -- desirable -- 5000kg/cm² the above -- further -- desirable -- 6000kg/cm² it is . It is 4000kg/cm² when it uses as a separator for cells. Below, it is inferior to assembly workability and productivity, and it is thought that practicality is low. Whenever [breaking extension / of the direction of a machine and the direction of a right angle (cross direction)] is 500% or more still more preferably 450% or more preferably 400% or more. Although a reason is not certain, if this elongation after fracture becomes 400% or less, when carrying out pleating of this fine porosity film with a nonwoven fabric, it becomes easy to split in the direction of a machine.

[0013] Moreover, if whenever [breaking extension] becomes 400% or less, by being in the inclination which the internal short circuit of a cell increases, and having moderate elongation crosswise at the time of cell assembly, although a reason is not certain, it will be hard to split in the direction of a machine, and it will be thought that a hole cannot become large easily. the bubble point in ethyl alcohol -- 2kg/cm² - 10kg/cm² -- desirable -- 3kg/cm² - 9kg/cm² -- further -- desirable -- 4kg/cm² - 8kg/cm² it is .

The bubble point in ethyl alcohol is 2kg/cm². Below, the aperture of the fine porosity film is large, and when it uses as a membrane filter, it worries about the leak of a bacillus, and when it uses especially for the separator of a lithium cell, it worries about generating of an internal short circuit. Moreover, the bubble point in ethyl alcohol is 10kg/cm². Above, when the aperture of the fine porosity film is too small and uses as a membrane filter, permeability becomes small, filtration effectiveness is bad, and when it uses as a separator for cells, there is a possibility of causing the fall of the impregnating ability of the electrolytic solution.

[0014] It is thought that the homogeneity of the internal resistance of a cell is required for reservation of safety, and in desiring fine porosity film homogeneous [when using as a membrane filter] in order to secure positive disinfection nature and using especially as a separator of a lithium cell, similarly, homogeneous fine porosity film is desired, and when the ratio of an average aperture and the maximum aperture becomes 1.6 or more, anxiety is in homogeneity. Preferably, it is 1.4 or less still more preferably 1.5 or less.

[0015] Although especially thickness is not specified in this invention, the point of the dependability as a membrane filter and the dependability as a separator for cells to 15 micrometers - 60 micrometers are desirable. 20 micrometers - 50 micrometers are 25 micrometers - 45 micrometers still more preferably more preferably. When set to 15 micrometers or less, it is the filtration precision of the direction of thickness.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, although an example explains this invention, this invention is not limited to the following example. In addition, a measuring method is shown below:

- (1) It measured with the dial gage of the 1 micrometer of the thickness minimum graduations.
- (2) The sample of a porosity the angle of 10cm was started, the weight and thickness at the time of the weight and the bone dry at the time of the water of a sample were measured, and it asked from the bottom type.

[0025] Porosity = (hole volume / fine porosity film volume) x100 (%)

Hole volume = ([wet weight g]-oven dry weight [g]) the consistency of /water [g/cm³]

Fine porosity film volume = 100x thickness [cm]

- (3) Bubble point ASTM The bubble point in ethanol was measured based on E-128-61.

(4) Air permeability JIS Based on P-8117, the time amount required by the marked-line graduations 0-100 was measured by the stopwatch using B mold gar rhe type Denso meter made from an Oriental energy machine.

(5) Using the form autograph AG-A mold by elastic-modulus Shimazu, the magnitude of a test piece performed the tension test in the distance between chucks of 5mm, and speed-of-testing 200 mm/min by width-of-face [of 10mm] x die length of 100mm, and measured the elastic modulus.

[0026] The cross section was computed by the thickness x film width measured by (1) term.

(6) Whenever [**** breaking extension], using the Shimazu form autograph AG-A mold, the magnitude of a test piece performed the tension test in the distance between chucks of 50mm, and speed-of-testing 200 mm/min by width-of-face [of 10mm] x die length of 100mm, calculated the amount of elongation from a chart to fracture, and computed by the bottom type.

[0027] It is =(amount [mm] of elongation-50[mm] to fracture)/50[mm] x100[%] whenever [**** breaking extension].

(7) Average aperture ASTM It asked by the half dry cleaning method based on F-316-70.

(8) The maximum aperture ASTM According to E-128-61, it computed from the bubble point in the inside of ethanol.

(9) Using the viscosity-average-molecular-weight decalin, viscosity was measured with the UBEROZE mold viscosity mold at the measurement temperature of 135 degrees C, and viscosity average molecular weight was calculated by the formula of Chiang.

[0028]

[Example 1] 17 % of the weight of ultra high molecular weight polyethylene, 18 % of the weight of fines silicic acid, 50 % of the weight of dioctyl phthalates, and 15 % of the weight of liquid paraffins of viscosity average molecular weight 3 million were mixed with the Henschel mixer, and the mixture concerned was fabricated by the film manufacturing installation which attached the T die of 450mm width of face in phi30mm twin screw extruder with a thickness of 200 micrometers in the shape of film.

[0029] The fabricated film was immersed for 10 minutes into 1,1,1-trichloroethane, after extracting dioctyl phthalate, it dried, it was immersed for 60 minutes into 60 more-degree C 25% caustic alkali of sodium, and after extracting fines silicic acid, it was dried. Furthermore, this fine porosity film was

extended so that thickness might be set to 30 micrometers - 40 micrometers by the heated 125-degree C 1 shaft roll drawing machine, and heat treatment was performed for 5 seconds under the 115-degree C ambient atmosphere.

[0030] The property of the obtained fine porosity film is shown in Table 1.

[0031]

[Example 2] It carried out like the example 1 except having used the ultra high molecular weight polyethylene of viscosity average molecular weight 2 million. The result is shown in Table 1.

[0032]

[Example 3] It carried out like the example 1 except 35 % of the weight of dioctyl phthalates, and 30 % of the weight of liquid paraffins. The result is shown in Table 1.

[0033]

[Example 4] It carried out like the example 1 except 57 % of the weight of dioctyl phthalates, and 8 % of the weight of liquid paraffins. The result is shown in Table 1.

[0034]

[Example 5] It carried out like the example 1 except having mixed 18 % of the weight of ultra high molecular weight polyethylene, 17 % of the weight of fines silicic acid, 48 % of the weight of dioctyl phthalates, and 17 % of the weight of liquid paraffins of viscosity average molecular weight 3 million with the Henschel mixer. The result is shown in Table 1.

[0035]

[The example 1 of a comparison] Other than 30 % of the weight of dioctyl phthalates, and 35 % of the weight of liquid paraffins, although it was going to carry out like the example 1, the miscibility in a Henschel mixer was bad and did not result in fabrication.

[0036]

[The example 2 of a comparison] It carried out like the example 1 except only the liquid paraffin having used 65 % of the weight as a plasticizer. The result is shown in Table 1.

[0037]

[The example 3 of a comparison] Fabrication was not able to be carried out although it was going to carry out like the example 1 except only dioctyl phthalate having used 65 % of the weight as a plasticizer.

[0038]

[The example 4 of a comparison] As a plasticizer, other than having used the acetyl tree n-butyl phthalate of the SP value 10.0 [about], although it was going to carry out like the example 1, fabrication was not able to be carried out instead of dioctyl phthalate.

[0039]

[The example 5 of a comparison] As a plasticizer, other than having used the G n-octyl tetrahydro phthalate of the SP value 7.2 [about], although it was going to carry out like the example 1, fabrication was not able to be carried out instead of the liquid paraffin.

[0040]

[The example 6 of a comparison] It carried out like the example 1 except having extended to biaxial this fine porosity film heated by 125 degrees C 3 time x 3 times using the tenter. The result is shown in Table 1.

[0041]

[Table 1]

	気孔率 (%)	透気度 (SEC/ 100CC)	M D 弹性率 (kg/cm ²)	CMD 破断伸度 (%)	バブル ポイント (kg/cm ²)	最大孔径 と平均 孔径比	膜 厚 (μm)
実施例1	72	180	8000	480	6.1	1.5	34
実施例2	72	180	7600	500	6.0	1.5	40
実施例3	65	170	8000	500	7.8	1.5	36
実施例4	70	170	7500	500	5.9	1.5	40
実施例5	68	170	8500	510	6.0	1.5	32
比較例1							
比較例2					10.0以上		
比較例3							
比較例4							
比較例5							
比較例6				300			

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(54)【発明の名称】 均質な超高分子量ポリエチレン製微多孔膜及びその製造方法

(57)【要約】

【目的】 高強度で、かつ適度な孔径を有した微多孔膜
を提供する。

【構成】 粘度平均分子量が200万以上の起高分子量
ポリエチレンからなる微多孔膜であって、機械方向に高
強度で、巾方向に適度な伸びを有した微多孔膜。

1

【特許請求の範囲】

【請求項1】 粘度平均分子量が、200万以上である超高分子量ポリエチレンからなる三次元網目構造を有する微多孔膜であって、気孔率が40%以上、透気度が450sec/100cc以下、機械方向の弾性率が4000kg/cm²以上、機械方向と直角方向の破断伸度が400%以上、エチルアルコールにおけるバブルポイントが2kg/cm²~10kg/cm²であり、平均孔径と最大孔径の比が、1.6以下であることを特徴とする均質な超高分子量ポリエチレン製微多孔膜。

【請求項2】 粘度平均分子量が、200万以上である超高分子量ポリエチレンと無機微粉体及び可塑剤の混合物を混練・加熱溶融しながらシート状に成形した後、無機微粉体及び可塑剤をそれぞれ抽出除去及び乾燥し、一軸方向のみに延伸して微多孔膜を得る製造方法において、該可塑剤のSP値が、7.5~8.4と8.5~9.5の少なくとも2種類の混合可塑剤を用い、かつSP値が7.5~8.4の可塑剤量が該ポリエチレン重量の10%~15%であることを特徴とする、気孔率が40%以上、透気度が450sec/100cc以下、機械方向の弾性率が4000kg/cm²以上、機械方向と直角方向の破断伸度が400%以上、エチルアルコールにおけるバブルポイントが2kg/cm²~10kg/cm²であり、平均孔径と最大孔径の比が、1.6以下である均質な超高分子量ポリエチレン製微多孔膜の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、超高分子量ポリエチレンからなる微多孔膜に関する。特に、本発明は三次元網目構造を有する均質な超高分子量のポリエチレン製微多孔膜に関する。

【0002】

【従来の技術】微多孔膜は、電池用セパレータ・電解コンデンサー用セパレータ・精密ろ過膜等として用いられている。電池用セパレータ・電解コンデンサー用セパレータには、電池・電解コンデンサーの組立加工性及び信頼性の点から強くて均質な微多孔膜が望まれており、特にリチウム電池などの非水電解液電池用のセパレータには、強くて均質で、かつ電気抵抗の小さな微多孔膜が要求されている。

【0003】また、精密ろ過膜には、適度な孔径を有した強くて均質な微多孔膜が望まれている。強い微多孔膜を製造するには、樹脂と溶媒によって多孔化する方法において、超高分子量のポリエチレンを使い、かつ延伸する方法が考えられる。例えば、特開昭60-24203号公報に開示されており、高強度ではあるが、平均貫通孔径が小さいため、浄水器などの多量の水をろ過する精密ろ過膜として適さないばかりでなく、電池用セパレータとして用いた場合、電解液の含浸性が悪い。また、可

2

塑剤抽出により成形シートが大幅に収縮し、2軸延伸しなければならないため、少なくとも一方の破断伸びが小さく、電池の組立加工性が悪いと考えられる。

【0004】さらに、特開昭60-136161号公報に開示されているように膜厚が薄いためにリチウム電池のセパレータとして用いるには、安全性の点から問題があった。また、特開昭63-273651号公報には、超高分子量ポリエチレンからなる比較的膜厚の厚い微多孔膜の製造方法が開示されているが、同様に高強度ではあるが、適度な孔径は有さず、透水度が小さく、多量の水などを処理する精密ろ過膜としては適さない。

【0005】他の微多孔膜の製造方法として、樹脂と可塑剤と充填剤からなる混合物の相分離後、可塑剤あるいは可塑剤と充填剤を抽出除去して多孔化する方法がある。例えば、特開昭55-165573号公報であるが、明細書中に記載されているように、一般的な手順及び材料に従って形成した微多孔膜は電気抵抗が高く、すなわち、水等の透過抵抗も高いと考えられ、適度な孔径は有さず、精密ろ過膜としては少なくとも適さず、電気抵抗が高いためセパレータにも適さないと考えられる。

【0006】さらに、特公昭45-32097号公報、特開平2-94356号公報などがあるが、いずれにおいても粘度平均分子量が200万以上の超高分子量製微多孔膜の製造方法に関しては開示されていない。これは、超高分子量になればなる程、成形加工が困難となり、一般的な方法では微多孔膜の製造ができなかつたためである。

【0007】また、超高分子量ポリエチレンと高分子量ポリエチレンの混合物からなる微多孔膜が、特開昭57-49629号公報、特開平2-21559号公報などが開示されているが、特開昭60-242035号公報と特開平3-105851号公報で比較されるように、一般的に混合物になると成形加工性は向上するが、微多孔膜の強さは著しく低下し、強い微多孔膜を得るには、好ましい方法ではない。

【0008】

【発明が解決しようとする課題】超高分子量のポリエチレンを用いることにより、高強度化は達成されるが、多量水ろ過用などの精密ろ過膜や安全性を必要とするリチウム電池用セパレータには、適度な孔径を有し、幅方向(機械方向と直角方向)に適度な破断伸度を有する微多孔膜が望まれている。しかしながら、超高分子量ポリエチレンの加工性の低さ等の問題から所期の微多孔膜は得られていなかった。

【0009】

【課題を解決するための手段】本発明者は、超高分子量のポリエチレン製微多孔膜において、高強度で、適度な孔径を有し、かつ均質である微多孔膜及びその製造方法を見いだし、本発明を完成した。すなわち、本発明は、粘度平均分子量が、200万以上の超高分子量ポリエチ

3

レンからなる三次元網目構造を有する微多孔膜であつて、気孔率が40%以上、透気度 $450\text{ sec}/100\text{ cc}$ 以下、機械方向の弾性率が 4000 kg/cm^2 以上、機械方向と直角方向の破断伸度が400%以上、エチアルアルコールにおけるバブルポイントが $2\text{ kg/cm}^2 \sim 10\text{ kg/cm}^2$ であり、平均孔径と最大孔径の比が1.6以下であることを特徴とする均質な超高分子量ポリエチレン製微多孔膜である。

【0010】本発明でいうところのポリエチレンとしては、粘度平均分子量が200万以上であり、エチレンを重合した結晶性の単独重合体もしくはエチレンと10モル%以下のプロピレン、1-ブテン、4-メチル-1-ペンテン、1-ヘキセンとの共重合体があげられる。三次元網目構造とは、三次元的に樹脂がネットワーク構造を有しており、その樹脂のネットワーク構造間が連通孔として孔を形成している構造を言う。

【0011】気孔率は、電池用セパレータとして用いた場合、電解液の含浸性及び電池の内部抵抗の観点から、40%以上であることが望ましく、さらには50%以上であることが望ましい。気孔率が85%以上になると微多孔膜の強度が低下し、取り扱い上不具合を生ずる。透気度は、 $450\text{ sec}/100\text{ cc}$ 以下、好ましくは $300\text{ sec}/100\text{ cc}$ 以下、さらに好ましくは $200\text{ sec}/100\text{ cc}$ 以下である。透気度が $450\text{ sec}/100\text{ cc}$ 以上では、電池用セパレータとして用いた場合、電池の内部抵抗が高くなりすぎ、電池特性を低下させ、精密ろ過膜として用いた場合、透水度が低くろ過効率が悪くなる。

【0012】機械方向（長手方向）の弾性率は、 4000 kg/cm^2 以上、好ましくは 5000 kg/cm^2 以上、さらに好ましくは 6000 kg/cm^2 である。電池用セパレータとして用いた場合、 4000 kg/cm^2 以下では、組立加工性・生産性に劣り、実用性が低いと考えられる。機械方向と直角方向（幅方向）の破断伸度は、400%以上、好ましくは450%以上、さらに好ましくは500%以上である。理由は定かではないが、該破断伸びが400%以下になると、該微多孔膜を不織布とともにプリーツ加工する場合など、機械方向に裂け易くなる。

【0013】また、破断伸度が400%以下になると、電池の内部短絡が増加する傾向にあり、理由は定かではないが、電池組立時において幅方向に適度な伸びを有することにより、機械方向に裂けにくく、孔が大きくなりにくいと思われる。エチアルアルコールにおけるバブルポイントは、 $2\text{ kg/cm}^2 \sim 10\text{ kg/cm}^2$ 、好ましくは $3\text{ kg/cm}^2 \sim 9\text{ kg/cm}^2$ 、さらに好ましくは $4\text{ kg/cm}^2 \sim 8\text{ kg/cm}^2$ である。エチアルアルコールにおけるバブルポイントが 2 kg/cm^2 以下では、微多孔膜の孔径が大きく、精密ろ過膜として用いた場合、菌のリークが心配され、特にリチウム電池のセパ

4

レータに用いた場合には、内部短絡の発生が心配される。また、エチアルアルコールにおけるバブルポイントが 10 kg/cm^2 以上では、微多孔膜の孔径が小さすぎて、精密ろ過膜として用いた場合、透水度が小さくなりろ過効率が悪く、電池用セパレータとして用いた場合、電解液の含浸性の低下を招く恐れがある。

【0014】精密ろ過膜として用いる場合には、確実な除菌性を確保するために均質な微多孔膜が望まれ、特にリチウム電池のセパレータとして用いる場合には、電池の内部抵抗の均一性が安全性の確保に必要だと考えられ、同様に、均質な微多孔膜が望まれ、平均孔径と最大孔径の比が1.6以上になると均質性に不安がある。好ましくは、1.5以下、さらに好ましくは、1.4以下である。

【0015】本発明において膜厚は特に規定していないが、精密ろ過膜としての信頼性及び電池用セパレータとしての信頼性の点から、 $15\mu\text{m} \sim 60\mu\text{m}$ が好ましい。より好ましくは、 $20\mu\text{m} \sim 50\mu\text{m}$ 、さらに好ましくは、 $25\mu\text{m} \sim 45\mu\text{m}$ である。 $15\mu\text{m}$ 以下になると膜厚方向のろ過精度（ディップス効果）に劣り、また電池用セパレータにおいては、内部短絡の心配がある。 $60\mu\text{m}$ 以上では、精密ろ過膜としては透水度が低下し、電池用セパレータとしては内部抵抗が増加するので、好ましくない。

【0016】本発明が開示するところの、粘度平均分子量が、200万以上の超高分子量ポリエチレンからなる三次元網目構造を有する微多孔膜であって、膜厚が $15\mu\text{m} \sim 60\mu\text{m}$ 、気孔率が40%以上、透気度が $450\text{ sec}/100\text{ cc}$ 以下、機械方向の弾性率が 4000 kg/cm^2 以上、機械方向と直角方向の破断伸度が400%以上、エチアルアルコールにおけるバブルポイントが $2\text{ kg/cm}^2 \sim 10\text{ kg/cm}^2$ であり、平均孔径と最大孔径の比が、1.6以下であることを特徴とする均質な超高分子量ポリエチレン製微多孔膜は、リチウム電池用セパレータとして最適である。

【0017】さらに、該微多孔膜表面に開孔している孔の形状については、梢円形が好ましいと考えられる。これは、精密ろ過膜として用いた場合、該微多孔膜表面の開孔が梢円形だと円形に比べ目詰まりしにくくろ過寿命が長いと思われ、該梢円形の長軸と短軸の比が1.3以上が好ましく、1.5以上がさらに好ましい。本発明の微多孔膜は、粘度平均分子量が、200万以上の超高分子量ポリエチレンと無機微粉体及び可塑剤の混合物を混練・加熱溶融しながらシート状に成形した後、無機微粉体及び可塑剤をそれぞれ抽出除去及び乾燥し、一軸方向のみに延伸して微多孔膜を得る製造方法において、該可塑剤のSP値が7.5~8.4と8.5~9.5の少なくとも2種類の混合可塑剤を用い、かつSP値が7.5~8.4の可塑剤量が該ポリエチレン重量の200%以下であることを特徴とする製造方法によって製造され

る。

【0018】また、単に選ばれた2種類以上の混合可塑剤では、強くて適度な孔径を有する微多孔膜は得られない。本発明で開示する特に選ばれた2種類以上の可塑剤を用い、かつ少なくとも1種類の可塑剤量を制限することにより、成形加工が容易で一軸方向のみの延伸によって、高強度かつ適度な孔径を有した精密ろ過膜・電池用セパレータ等に適した均質な超高分子量ポリエチレン製微多孔膜が得られる。一軸方向のみの延伸で適度な孔径を有し、かつ延伸方向に特に高強度な微多孔膜が得られることは、工業生産上経済性が高いばかりでなく、幅方向(延伸方向の直角方向)に適度な破断伸びを有しているため、機械方向に裂けにくいと言う特徴を有する。

【0019】具体的には、ポリエチレン、可塑剤、無機微粉体を混合、成形後抽出及び乾燥し、さらに延伸することにより製造する。無機微粉体としては、微粉珪酸、珪酸カルシウム、珪酸アルミニウム、炭酸カルシウム、微粉タルク等が上げられる。例えば、ポリエチレン、無機微粉体、可塑剤の混合組成をそれぞれ10~40重量%、5~35重量%、20~80重量%とし、ヘンシェルミキサー等の通常の混合機で混合した後、押し出し機等の溶融混練装置により混練し、得られた混練物を押し出し成形等により80μm~600μmの厚さに成形する。さらに、該成形物から溶剤を用いて可塑剤を抽出除去し、続いて無機微粉体の抽出溶剤にて無機微粉体を抽出した後、一軸方向のみの延伸でもすぐれた微多孔膜が得られる。

【0020】可塑剤の溶剤としては、メタノール、エタノール等のアルコール類、アセトン、MEK等のケトン類、1,1,1-トリクロロエタン等の塩素系炭化水素等一般的な有機溶剤が用いられる。本発明に用いられるSP値が7.5~8.4の可塑剤としては、流動バラフィン、プロセスオイル等の鉱物油等が上げられる。

【0021】また、SP値が8.5~9.5の可塑剤としては、DBP、DOP、DNP、DBS、TBP等が上げられる。SP値が7.5~8.4の可塑剤量は、ポリエチレン重量の5%から200%、好ましくは15%~150%、さらに好ましくは35%~100%、最も好ましくは50%~100%である。該可塑剤量が200%以上になると、適度な孔径を有する微多孔膜が得られず、5%以下では、成形性が悪く製造が困難である。

【0022】該混合可塑剤の量は、混合性及び適度な孔径を有する為にも、該混合物(ポリエチレン・可塑剤・無機微粉体)重量の50%~180%、好ましくは55%~150%、さらに好ましくは60%~120%である。該混合可塑剤量が50%以下では、適度な孔径の微多孔膜は得られず、180%以上になるとポリエチレン・可塑剤・無機微粉体の混合性が低下し成形加工が困難となる。

【0023】また、延伸は一軸方向にのみ延伸する必要

がある。当然のことながら二軸延伸することも可能であるが、幅方向に適度な破断伸びが得られないと言う問題がある。

【0024】

【実施例】以下、実施例により本発明を説明するが、本発明は下記実施例に限定されるものではない。なお、測定方法を下記に示す。

(1) 膜厚

最小目盛り1μmのダイヤルゲージにて測定した。

10 (2) 気孔率

10cm角のサンプルを切り出し、サンプルの含水時の重量・絶乾時の重量及び膜厚を測定し、下式から求めた。

$$\text{【0025】} \text{ 気孔率} = (\text{空孔容積}/\text{微多孔膜容積}) \times 100 (\%)$$

$$\text{空孔容積} = (\text{含水重量} [\text{g}] - \text{絶乾重量} [\text{g}]) / \text{水の密度} [\text{g}/\text{cm}^3]$$

$$\text{微多孔膜容積} = 100 \times \text{膜厚} [\text{cm}]$$

(3) バブルポイント

20 ASTM E-128-61に準拠し、エタノール中のバブルポイントを測定した。

(4) 透気度

JIS P-8117に準拠し、東洋精機製B型ガーレー式デンソーメータを用い、標線目盛0~100までに要する時間をストップウォッチで測定した。

(5) 弹性率

島津社製の型式オートグラフAG-A型を用いて、試験片の大きさが幅10mm×長さ100mmでチャック間距離5mm、引張速度200mm/minにおいて引張試験を行い、弾性率を測定した。

【0026】断面積は、(1)項で測定した膜厚×膜幅によって算出した。

(6) 引張破断伸度

島津社製の型式オートグラフAG-A型を用いて、試験片の大きさが幅10mm×長さ100mmでチャック間距離50mm、引張速度200mm/minにおいて引張試験を行い、チャートから破断までの伸び量を求め、下式により算出した。

$$40 \text{ 【0027】} \text{ 引張破断伸度} = (\text{破断までの伸び量} [\text{mm}] - 50 [\text{mm}]) / 50 [\text{mm}] \times 100 [\%]$$

(7) 平均孔径

ASTM F-316-70に準拠したハーフドライ法によって求めた。

(8) 最大孔径

ASTM E-128-61に準じて、エタノール中のバブルポイントより算出した。

(9) 粘度平均分子量

デカリニを用い、測定温度135°Cでウベローゼ型粘度型により粘度を測定し、Chiangの式により粘度平均分子量を求めた。

【0028】

【実施例1】粘度平均分子量300万の超高分子量ポリエチレン17重量%と微粉珪酸18重量%とジオクチルフタレート50重量%及び流動パラフィン15重量%をヘンシェルミキサーで混合し、当該混合物をφ30mm二軸押出機に450mm幅のTダイを取り付けたフィルム製造装置で厚さ200μmの膜状に成形した。

【0029】成形された膜は、1, 1, 1-トリクロルエタン中に10分間浸漬し、ジオクチルフタレートを抽出した後乾燥し、さらに60℃の25%苛性ソーダ中に60分間浸漬して、微粉珪酸を抽出した後乾燥した。さらに、該微多孔膜を125℃の加熱された一軸ロール延伸機により膜厚が30μm～40μmになるように延伸し、115℃の雰囲気下で5秒間熱処理を行った。

【0030】得られた微多孔膜の特性を表1に示す。

【0031】

【実施例2】粘度平均分子量200万の超高分子量ポリエチレンを用いた以外は、実施例1と同様に行った。その結果を表1に示す。

【0032】

【実施例3】ジオクチルフタレート35重量%、流動パラフィン30重量%以外は、実施例1と同様に行った。その結果を表1に示す。

【0033】

【実施例4】ジオクチルフタレート57重量%、流動パラフィン8重量%以外は、実施例1と同様に行った。その結果を表1に示す。

【0034】

【実施例5】粘度平均分子量300万の超高分子量ポリエチレン18重量%と微粉珪酸17重量%とジオクチルフタレート48重量%及び流動パラフィン17重量%を

10 ヘンシェルミキサーで混合した以外は、実施例1と同様に行った。その結果を表1に示す。

【0035】

【比較例1】ジオクチルフタレート30重量%、流動パラフィン35重量%以外は、実施例1と同様に実施しようとしたが、ヘンシェルミキサーでの混合性が悪く、成形加工に至らなかった。

【0036】

【比較例2】可塑剤として流動パラフィンのみ65重量%を用いた以外は、実施例1と同様に行った。その結果を表1に示す。

【0037】

【比較例3】可塑剤としてジオクチルフタレートのみ65重量%を用いた以外は、実施例1と同様に実施しようとしたが、成形加工できなかった。

【0038】

【比較例4】可塑剤として、ジオクチルフタレートの代わりに、SP値約10.0のアセチル・トリーナ-ブチルフタレートを用いた以外は、実施例1と同様に実施しようとしたが、成形加工できなかった。

【0039】

【比較例5】可塑剤として、流動パラフィンの代わりに、SP値約7.2のジーノ-オクチルテトラヒドロフタレートを用いた以外は、実施例1と同様に実施しようとしたが、成形加工できなかった。

【0040】

【比較例6】125℃に加熱された該微多孔膜をテンタ一を用いて2軸に3倍×3倍延伸した以外は、実施例1と同様に行った。その結果を表1に示す。

【0041】

【表1】

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	気孔率 (%)	透気度 (SEC/ 1000C)	M D 弾性率 (kg/cm ²)	CMD 破断伸度 (%)	バブル ポイント (kg/cm ²)	最大孔径 と平均 孔径比	膜厚 (μm)
実施例1	72	180	8000	480	6.1	1.5	34
実施例2	72	180	7600	500	6.0	1.5	40
実施例3	65	170	8000	500	7.8	1.5	36
実施例4	70	170	7500	500	5.9	1.5	40
実施例5	68	170	8500	510	6.0	1.5	32
比較例1							
比較例2					10.0以上		
比較例3							
比較例4							
比較例5							
比較例6				300			

【0042】

【発明の効果】上記構成によれば、高強度で適度な孔径を有する微多孔膜が得られ、特に精密ろ過膜としては、均質であり信頼性の高いろ過膜として、特に非水電解液*

*電池用セパレータとして、加工性・安全性が高く、低内部抵抗で、かつ均一な低内部抵抗の特性を有するセパレータとして適用できる。